



Research Paper

Formation of N₂O greenhouse gas during SCR of NO with NH₃ by supported vanadium oxide catalysts

Minghui Zhu, Jun-Kun Lai, Israel E. Wachs*

Operando Molecular Spectroscopy & Catalysis Laboratory, Department of Chemical & Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States

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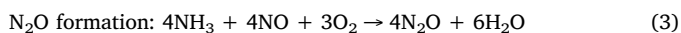
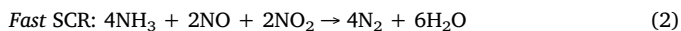
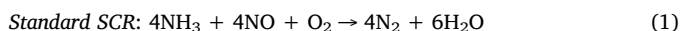
N₂O
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 Isotopic study
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ABSTRACT

Selective catalytic reduction of NO by NH₃ over supported vanadium oxide catalysts has been studied for decades, but the studies mostly concentrated on the dominant N₂ product with much less attention paid to the formation of the undesired N₂O product. In the present study, fundamental aspects of the N₂O formation reaction were elucidated by a series of temperature-programmed surface reaction studies with isotopic labelled reactants. The surface vanadium oxide species on the TiO₂ support are active sites for the N₂O formation reaction, while tungsten species mainly function as promoters. Oxygen from NO, gaseous O₂ and catalyst oxygen all function as oxygen sources for formation of N₂O (~50%, ~30% and ~20%, respectively). The rate-determining-step for N₂O formation involves breaking of the ammonia N–H bond. These new molecular level insights have the potential to guide the rational design of improved SCR catalysts for diesel engines with reduced N₂O produced.

1. Introduction

Nitrous Oxide (N₂O) is a non-CO₂ greenhouse gas that has up to 300 times higher greenhouse forcing effect compared to CO₂ and is considered as the dominant stratospheric ozone-depleting substance being emitted in the 21 st century [1–3]. Although N₂O comes predominantly from natural sources (~60%) such as vegetation containing soils, bacteria and fungi in oceans and atmospheric chemical reactions such as lightening [4], the transportation sector is still considered as a significant anthropogenic source of N₂O emissions with 56 mg of N₂O/km of travel being produced from on-road vehicles [5]. As a result, N₂O from diesel engine emissions has recently started to be regulated [6].



The selective catalytic reduction (SCR) of NO_x with ammonia by supported V₂O₅-WO₃/TiO₂ catalysts is a widely utilized NO_x abatement technology for stationary sources and mobile diesel vehicles [7–12]. Depending on the reactants, “standard” SCR (Eq. (1)) and “fast” SCR (Eq. (2)) can take place with the former reaction predominant as NO₂ only contributed to 5–15% of the total NO_x emissions from diesel engines [13]. The NH₃-SCR catalytic reaction has been extensively studied over several decades, but the mechanism and kinetics for the N₂O

formation side reaction (Eq. (3)) has received limited attention in only a few reports because most of the papers focused on the desired and predominant N₂ product [8–12,14–21]. From steady-state isotopically labelled experiments with ¹⁵N₂O and ¹⁴NH₃, it was found that N₂O forms by reaction between one NH₃ molecule and one NO molecule [22–24]. The source of the oxygen atom in N₂O was also previously discussed in the literature based on steady-state SCR reaction studies with isotopically labelled reactants (¹⁸O₂, ¹⁵N¹⁶O and ¹⁵N¹⁸O). It was observed that oxygen atoms of N₂O tracked by NO, O₂ and bulk O and was attributed to oxygen scrambling of NO and O₂ with the catalyst [22–26]. The oxygen scrambling, however, was only experimentally confirmed with a supported V₂O₅/TiO₂ catalyst in the absence of gas phase NH₃ [23]. The N₂O and N₂ formation pathways were also proposed to proceed from one common surface intermediate (NH_xNO) that dehydrogenates to N₂O under dry conditions and dehydrates to N₂ under wet conditions based on the suppression of N₂O formation by moisture [27]. This mechanism, however, is untenable since H₂O is also known to suppress the SCR reaction for N₂ formation [28]. An alternative mechanism proposed that N₂O formation proceeds by reaction between surface NH_{ads} and/or NH_{2,ads} species and adsorbed NO to yield N₂O, but supporting experimental evidence was not provided [25,29,30]. Thus, there are many critical unresolved questions regarding N₂O formation during the SCR of NO with NH₃ by supported vanadium oxide catalysts: active sites, reaction pathway(s), rate-determining-step, etc. In addition, previous studies only examined supported V₂O₅/TiO₂ catalysts, whereas, in the present study the state-of-art supported V₂O₅-WO₃/

* Corresponding author.

E-mail address: iew0@lehigh.edu (I.E. Wachs).

TiO₂ catalyst is also investigated. In order to resolve the fundamental aspects of this critical environmental catalytic reaction, a series of temperature-programmed surface reaction (TPSR) studies with isotopically labelled molecules (¹⁸O₂, H₂¹⁸O, ¹⁵N¹⁸O and ND₃) and catalysts (surface V = ¹⁸O) with the aid of *in situ* spectroscopy were undertaken.

2. Experimental details

2.1. Catalyst preparation

The catalysts were synthesized by the co-precipitation method. Metatitanic acid was precipitated from titanium isopropoxide (Ti(O-*i*-Pr)₄, Alfa Aesar, 99.999%) by addition of deionized water (molar ratio water/titanium isopropoxide = 110). After 60 min of stirring, the solution was filtered. The powder was washed and finally dried at 120 °C for 6 h. The obtained powder was then added to appropriate amount of deionized water to obtain a TiO(OH)₂ slurry with a concentration of 2 mol/L. Afterwards, aqueous solutions of ammonium metatungstate (Pfaltz & Bauer, 99.5% purity; 0.06 M) and (or) ammonium metavanadate (Aldrich; 0.35 M) were poured into the TiO(OH)₂ suspension. Into this mixed suspension, a solution of aqueous ammonia (Fisher Scientific) was gradually added dropwise with stirring to obtain the desired pH value of approximately 8 to produce a co-precipitate gel. The water was removed from the gel by evaporation in a water bath. Each sample was dried at 120 °C overnight, and then calcined at 450 °C for 4 h in air.

2.2. Temperature-programmed surface reaction (TPSR) spectroscopy

Temperature programmed studies were performed using an Altamira AMI-200 system equipped with an online quadrupole mass spectrometer (Dycor Dymaxion DME200MS). 50 mg of catalyst was loaded into a U-type quartz tube and initially treated in flowing 5% O₂/He to 500 °C (30 ml/min; heating rate of 10 °C/min) for 60 min and cooled to 50 °C. After the O₂ treatment, different sets of isotopically labelled SCR reaction mixtures were introduced (a) 35 ml/min of 2000 ppm NH₃/He, 35 ml/min of 2000 ppm ¹⁴N¹⁶O/He and 5 ml/min of 5% ¹⁶O₂/He; (b) 35 ml/min of 2000 ppm ND₃/He, 35 ml/min of 2000 ppm ¹⁴N¹⁶O/He and 5 ml/min of 5% ¹⁶O₂/He; (c) 35 ml/min of 2000 ppm NH₃/He, 35 ml/min of 2000 ppm ¹⁴N¹⁶O/He and 5 ml/min of 5% ¹⁸O₂/He and (d) 35 ml/min of 2000 ppm NH₃/He, 35 ml/min of 2000 ppm ¹⁵N¹⁸O/He and 5 ml/min of 5% ¹⁶O₂/He, then the sample was heated up to 500 °C at a rate of 10 °C/min. For the [¹⁴N¹⁶O + NH₃ + ¹⁶O₂]-TPSR after H₂¹⁸O pretreatment, the catalyst was exposed to 20 ml/min of He bubbling through a H₂¹⁸O (Sigma Aldrich, ISOTEC; 99% chemical purity; 97% atom purity) saturator for 1 h at 400 °C before cooling down in flowing Helium to 50 °C. Isotope reagents with desired concentration were prepared from diluting ND₃ (Sigma Aldrich, ISOTEC; 99% chemical purity; 99% atom purity), ¹⁸O₂ (Sigma Aldrich, ISOTEC; 99% chemical purity; 97% atom purity) and ¹⁵N¹⁸O (Sigma Aldrich, ISOTEC; 99% chemical purity; 98% N atom purity, 95% O atom purity).

3. Results and discussions

For the supported catalysts used in the present study (1 wt.% V₂O₅/TiO₂ (1VTi), 5 wt.% WO₃/TiO₂ (5WTi) and 1 wt.% V₂O₅-5 wt.% WO₃/TiO₂ (1V5WTi)), our previous characterization studies have confirmed with *in situ* Raman spectroscopy that only dispersed surface vanadia and tungsta phases were present on the TiO₂ support and, thus, neither crystalline V₂O₅ nor WO₃ nanoparticles were present [31,32]. The reactants and products during TPSR were continuously monitored with an online mass spectrometer (MS) and the results with unlabeled reactants are shown in Fig. 1(a). As the temperature increases, the reactants of NO, NH₃ and O₂ are consumed with the products of N₂ and H₂O starting

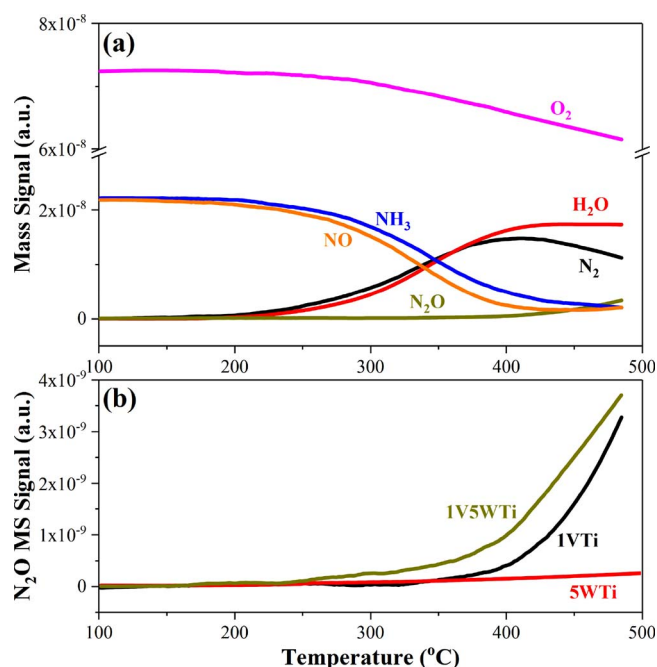


Fig. 1. MS signals for (a) N₂, H₂O, N₂O, NH₃, NO and O₂ during [¹⁴N¹⁶O + ¹⁴NH₃ + ¹⁶O₂]-TPSR on supported 1VTi; (b) N₂O during [¹⁴N¹⁶O + NH₃ + ¹⁶O₂]-TPSR on supported 1VTi, 5WTi and 1V5WTi.

to form at ~150 °C. The responses of the MS signals for evolution of H₂O and NH₃ are slightly delayed compared to N₂ and NO, respectively, because of the longer residence times of H₂O and NH₃ in the catalyst bed and capillary tube to the MS spectrometer due to their greater interactions related to adsorption-desorption processes. At ~400 °C, N₂ signal begins to decrease with a concomitant increase in N₂O signal, in agreement with the literature that N₂O starts to be formed at a temperature higher than 400 °C. The MS signals of N₂O over the three catalysts are compared in Fig. 1(b). The supported 5WTi catalyst didn't produce any N₂O up to 500 °C, indicating that surface WO_x species are not the active sites for N₂O formation at studied temperatures. Both V-containing supported 1VTi and 1V5WTi catalysts are active for the production of N₂O above 400 °C. The supported 1V5WTi catalyst, which is known to exhibit higher SCR activity than the supported 1VTi catalyst, also appears to be more active for N₂O formation [32]. The activation energy values for N₂O formation on the supported 1VTi and 1V5WTi catalysts were calculated using the transient MS signals for N₂O production over the temperature range of 450–485 °C (Fig. S1). The activation energy for the supported 1V5WTi catalyst is 52 ± 6 kJ/mol and is much lower than that of the supported 1VTi (72 ± 8 kJ/mol) catalyst. Comparison of the N₂O formation kinetics among the supported 1VTi, 5WTi and 1V5WTi catalysts demonstrates that surface VO_x are the active sites responsible for N₂O formation during the SCR reaction, and surface WO_x species are not active but can function as promoters for the supported VO_x-WO_x/TiO₂ catalysts.

A series of temperature-programmed experiments with isotopically labelled molecules were performed to obtain fundamental insights about the reaction pathways for N₂O formation during SCR. The MS signals of N₂O produced during [¹⁵N¹⁸O + ¹⁴NH₃ + ¹⁶O₂]-TPSR are presented in Fig. 2. Only the isotopomers ¹⁴N¹⁵N¹⁶O (*m/z* = 45) and ¹⁴N¹⁵N¹⁸O (*m/z* = 47) were evolved demonstrating that N₂O is formed by reaction between one NO molecule and one NH₃ molecule as was previously reported. The absence of ¹⁴N₂¹⁶O (*m/z* = 44) and ¹⁴N₂¹⁸O (*m/z* = 46) rules out an N₂O reaction pathway proceeding via oxidation of two ¹⁴NH₃ molecules.

Additional isotope-containing TPSR experiments were designed to obtain further insights into the oxygen sources for the N₂O formation pathways. The [¹⁴N¹⁶O + ¹⁴NH₃ + ¹⁸O₂]-TPSR and the [¹⁴N¹⁶O

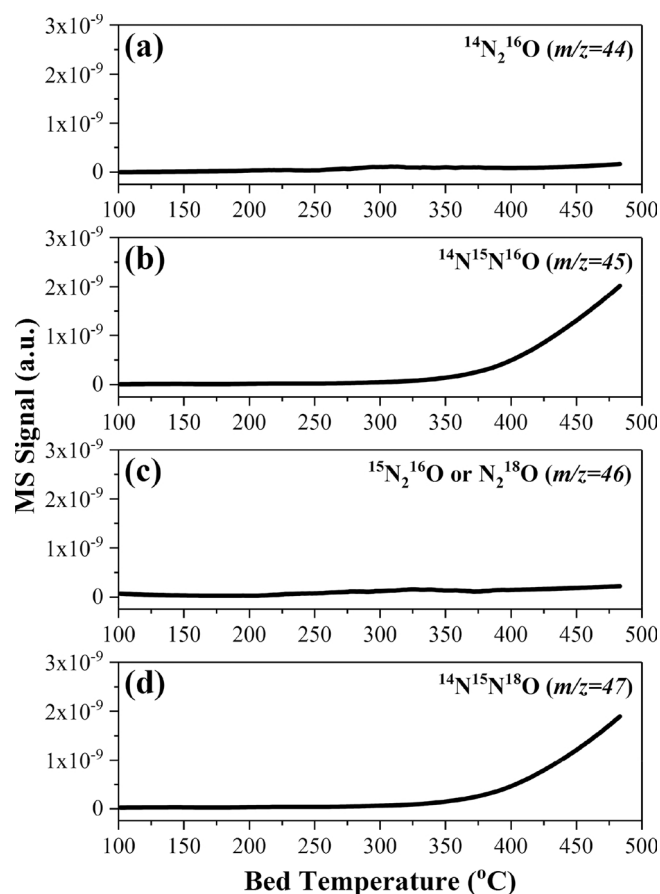


Fig. 2. MS signals of $^{14}\text{N}_2^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}_2^{16}\text{O}$, $^{14}\text{N}_2^{18}\text{O}$ and $^{14}\text{N}^{15}\text{N}^{18}\text{O}$ during $[^{15}\text{N}^{18}\text{O} + ^{14}\text{NH}_3 + ^{16}\text{O}_2]$ -TPSR for supported 1V5WTi catalyst.

+ $^{14}\text{NH}_3 + ^{16}\text{O}_2$]-TPSR on H_2^{18}O -pretreated catalyst (known to replace ^{16}O for the surface VO_x sites by ^{18}O)[32] formed both the N_2^{16}O and N_2^{18}O isotopomers during the two experiments (Fig. S2). The percentage of N_2^{18}O among all N_2O products, $\text{N}_2^{18}\text{O}/(\text{N}_2^{16}\text{O} + \text{N}_2^{18}\text{O})$, produced in the 400–500 °C temperature range is presented in Fig. 3 as a function of temperature. During $[^{15}\text{N}^{18}\text{O} + ^{14}\text{NH}_3 + ^{16}\text{O}_2]$ -TPSR and $[^{14}\text{N}^{16}\text{O} + ^{14}\text{NH}_3 + ^{18}\text{O}_2]$ -TPSR, the percentage of N_2^{18}O remained constant at ~50% and ~30%, respectively. The evolution of the isotopomers of the NO and O_2 gases during the $[^{14}\text{N}^{16}\text{O} + ^{14}\text{NH}_3 + ^{18}\text{O}_2]$ -TPSR are presented in Fig. S3. The absence of $^{16}\text{O}^{18}\text{O}$, $^{16}\text{O}_2$ and $^{14}\text{N}^{18}\text{O}$ isotopomers demonstrates that no significant NO or O_2 scrambling takes place under SCR reaction conditions. Thus, NO and O_2 both contribute to the oxygen atom of N_2O with NO contributing ~50% and O_2 contributing ~30%. The remaining ~20% comes from the catalyst oxygen (surface VO_x sites and TiO_2) that is consistent with $[^{14}\text{N}^{16}\text{O} + \text{NH}_3 + ^{16}\text{O}_2]$ -TPSR on the H_2^{18}O -pretreated catalyst where the percentage of N_2^{18}O drops from ~35% to ~10% as the reaction temperature increases. The decreasing percentage is due to the diminishing amount of available surface ^{18}O atoms due to the continuous consumption.

The scrambling of oxygen from NO, O_2 reactants as well as the catalyst surface towards was previously observed on supported VO_x/TiO_2 catalysts in the absence of NH_3 [23]. The current study involving isotopically labelled oxygen during the SCR reaction reveals that there is no oxygen exchange between molecular O_2 with the catalyst since the isotopomers $^{18}\text{O}^{16}\text{O}$ product is never detected (Fig. S3). Similarly, N^{18}O is not detected during SCR of N^{16}O and $^{18}\text{O}_2$ with ammonia (Fig. S3). Furthermore, the relative contributions of oxygen from NO, O_2 and the catalyst during the SCR reaction were quantified (~50%, ~30% and ~20%, respectively).

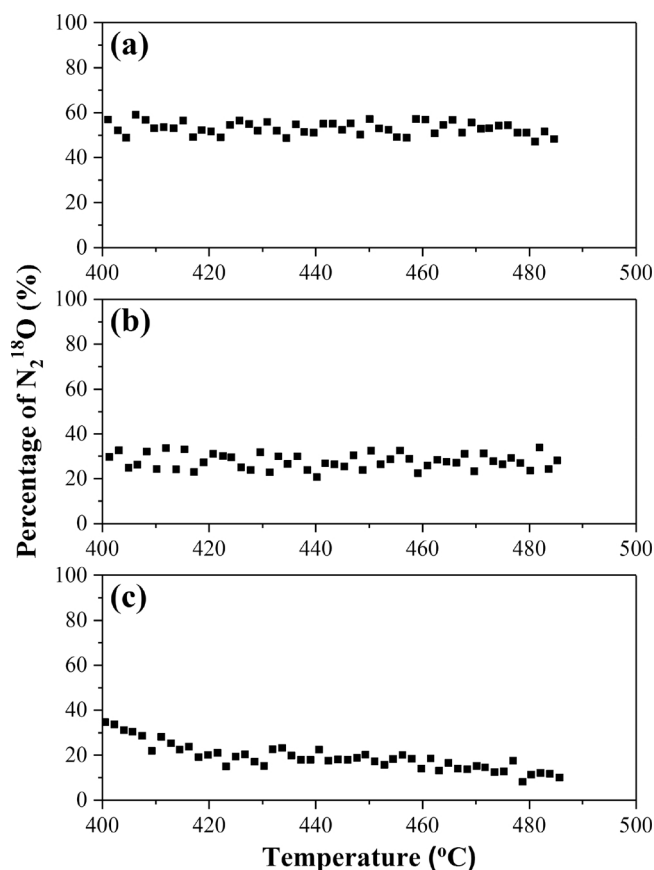


Fig. 3. Percentage of N_2^{18}O evolved among N_2O reaction products during a) $[^{15}\text{N}^{18}\text{O} + ^{14}\text{NH}_3 + ^{16}\text{O}_2]$ -TPSR; b) $[^{14}\text{N}^{16}\text{O} + ^{14}\text{NH}_3 + ^{18}\text{O}_2]$ -TPSR and c) $[^{14}\text{N}^{16}\text{O} + ^{14}\text{NH}_3 + ^{16}\text{O}_2]$ -TPSR after H_2^{18}O pretreatment of the supported 1V5WTi catalyst.

The rate-determining-step for N_2O formation by the supported 1V5WTi catalyst can also be evaluated by probing for Kinetic Isotope Effects (KIE) during TPSR with judiciously designed isotopically labelled experiments: 1) $[^{14}\text{N}^{16}\text{O} + \text{NH}_3 + ^{16}\text{O}_2]$ -TPSR as reference; 2) $[^{14}\text{N}^{16}\text{O} + \text{ND}_3 + ^{16}\text{O}_2]$ -TPSR to evaluate N–H bond breaking; 3) $[^{15}\text{N}^{18}\text{O} + ^{14}\text{NH}_3 + ^{16}\text{O}_2]$ -TPSR to evaluate N–O bond breaking; 4) $[^{14}\text{N}^{16}\text{O} + ^{14}\text{NH}_3 + ^{18}\text{O}_2]$ -TPSR to evaluate O–O bond breaking; 5) $[^{14}\text{N}^{16}\text{O} + ^{14}\text{NH}_3 + ^{16}\text{O}_2]$ -TPSR after H_2^{18}O pretreatment to evaluate V–O bond breaking. The formation of N_2O with the different isotopic labels is presented in Fig. 4 and follows quite similar trends with the only exception when ND_3 is the reactant. This TPSR experiment reveals that in the presence of the ND_3 the N_2O formation is significantly retarded and requires higher temperatures to proceed, demonstrating a kinetic isotope effect involving N–H/N–D bond breaking as the rate-determining-step. The N_2O evolution at different temperatures also allows determining the influence of the isotopomers upon the apparent activation energy for N_2O formation within the 450–485 °C range and the apparent E_{act} values are presented in Table S1. In the absence of any isotopic labels, the apparent E_{act} is ~52 kJ/mol. In the presence of isotopes for $^{18}\text{O}_2$, $^{15}\text{N}^{18}\text{O}$ and surface ^{18}O , the apparent E_{act} values vary from ~49–55 kJ/mol that are within experimental error. The expected KIE values for the non- ND_3 isotopes are only ~1.1 and the corresponding KIE values at 450 °C were determined to be ~1. There is, thus, no supporting evidence that the reaction steps of breaking O–O, N–O and V–O bonds are involved in the rate-determining-steps of the N_2O formation reaction. In the presence of ND_3 , however, the apparent activation energy significantly increases to 82 kJ/mol and the KIE at 450 °C is ~2.7. Both the higher apparent E_{act} and much lower rate for N_2O formation when NH_3 is substituted by ND_3 indicate that N–H bond breaking is the rate-determining-step of the N_2O formation during SCR

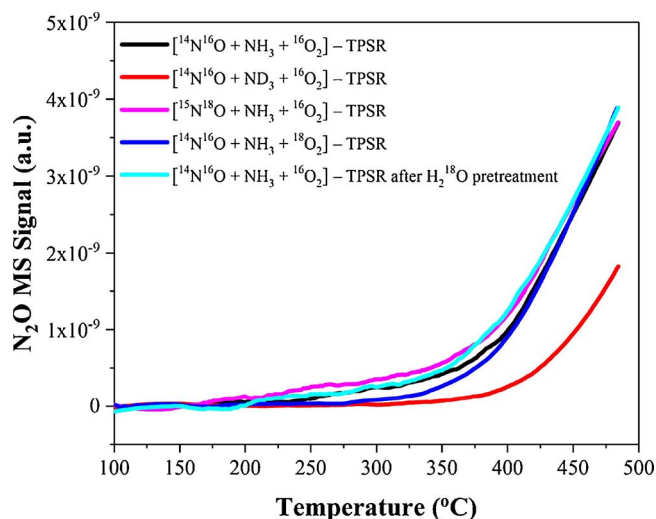


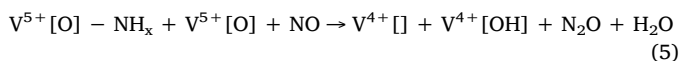
Fig. 4. MS signal of N₂O formed during TPSR on 1V5WTi with various isotopically labelled reactants.

of NO with NH₃ by titania-supported vanadia-tungsta catalysts.

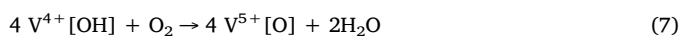
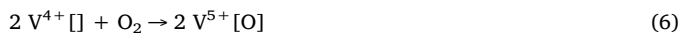
Based on the above new insights, the reaction pathway for N₂O formation during NH₃-SCR of NO by titania supported vanadium oxide catalysts can now be proposed. We already know that the surface VO_x species in V₂O₅-WO₃-TiO₂ catalyst are present as both Brønsted and Lewis acid sites forming surface NH₄⁺_{ads} and NH_{3,ads} species, respectively [33]. At the high temperatures where N₂O is formed, the surface contains a low concentration of ammonia species and is essentially fully oxidized. It's well established that the presence of water greatly suppresses the formation of N₂O [25,27] and also transforms surface Lewis acid sites into surface Brønsted acid sites [33]. Thus, we hypothesize that surface vanadium Lewis acid sites (V⁵⁺) are more active than vanadium Brønsted acid sites (V⁵⁺H) for N₂O formation. The first step in the catalytic active cycle involves adsorption of NH₃:



The absence of IR detectable surface NH_x species prevents identification of the specific NH_x intermediates during SCR. At high SCR reaction temperatures, less reducing surface NH₂ and NH species may also be present and may account for the formation of N₂O vs. N₂ during SCR. The isotope experiments demonstrate that N₂O is formed by the reaction between one NH₃ molecule and one NO molecule. The surface [NH_xNO] reactive intermediates is not IR observable because of the low concentration and short lifetime of such possible intermediates at the high temperatures where N₂O is formed. The formation of N₂O involves the participation of surface oxygen from the catalyst since the isotopic labeling experiments reveal that ~40% of the oxygen from the catalyst and molecular O₂, [catalyst oxygen/(catalyst oxygen + O₂)], is involved in the formation of the N₂O product. The isotopic studies also revealed that the rate-determining-step (rds) involves breaking of the N–H bond.



The reduced vanadium oxide sites are subsequently re-oxidized by gaseous O₂ to close the redox cycle and contributes to ~60% of the oxygen consumed since the isotopic labeling experiments reveal that ~60% of the oxygen from the catalyst and molecular O₂, [O₂/(catalyst oxygen + O₂)], is involved in the formation of N₂O. Through this step, molecular O₂ replenishes the surface oxygen vacancy.



4. Conclusions

In conclusion, application of a series temperature-programmed studies with isotopically labelled molecules (¹⁸O₂, H₂¹⁸O, ¹⁵N¹⁸O, ND₃) allowed direct demonstration of many new fundamental insights about the formation pathway and rate-determining-step of the N₂O side reaction during SCR of NO with NH₃ by titania-supported vanadia-tungsta catalysts: (1) surface VO₄ species are the catalytic active sites while surface WO_x species are not active and only act as promoters, (2) formation of N₂O involves one NH₃ molecule and one NO molecule, (3) NO, molecular O₂ and oxygen from the catalyst all contribute oxygen to the formation of N₂O (~50%, ~30% and ~20%, respectively), and (4) the rate-determining-step was for the first time shown to involve breaking of the ammonia N–H bond. The new fundamental understanding of N₂O formation mechanism has the potential to guide the rational design of improved catalysts for the reduction of toxic acidic NO_x emissions from diesel engine vehicles.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.11.029>.

References

- [1] H. Arakawa, M. Aresta, J.N. Armor, M.A. Barteau, E.J. Beckman, A.T. Bell, J.E. Bercaw, C. Creutz, E. Dinjus, D.A. Dixon, K. Domen, D.L. DuBois, J. Eckert, E. Fujita, D.H. Gibson, W.A. Goddard, D.W. Goodman, J. Keller, G.J. Kubas, H.H. Kung, J.E. Lyons, L.E. Manzer, T.J. Marks, K. Morokuma, K.M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielsen, W.M.H. Sachtler, L.D. Schmidt, A. Sen, G.A. Somorjai, P.C. Stair, B.R. Stults, W. Tumas, Catalysis research of relevance to carbon management: progress, challenges, and opportunities, *Chem. Rev.* 101 (2001) 953–996, <http://dx.doi.org/10.1021/cr000018s>.
- [2] A.L. Marten, S.C. Newbold, Estimating the social cost of non-CO₂ GHG emissions: methane and nitrous oxide, *Energy Policy* 51 (2012) 957–972, <http://dx.doi.org/10.1016/j.enpol.2012.09.073>.
- [3] A.R. Ravishankara, J.S. Daniel, R.W. Portmann, Nitrous oxide (N₂O): the dominant ozone-depleting substance emitted in the 21 st century, *Science* (80-.). 326 (2009) 123–125, <http://dx.doi.org/10.1126/science.1176985>.
- [4] B. Anderson, K. Barlett, S. Frohling, K. Hayhoe, J. Jenkins, W. Salas, Methane and nitrous oxide emissions from natural sources, U. S. Environ. Prot. Agency (2010) 1–194 EPA430-R-10-001.
- [5] K.H. Becker, R. Kurtenbach, P. Wiesen, T.E. Jensen, T.J. Wallington, Nitrous oxide (N₂O) emissions from vehicles, *Environ. Sci. Technol.* 33 (1999) 4134–4139, <http://dx.doi.org/10.1021/es9903330>.
- [6] C. Lambert, D. Dobson, C. Gierczak, G. Guo, J. Ura, J. Warner, Nitrous oxide emissions from a medium-duty diesel truck exhaust system, *Int. J. Powertrains* 3 (2014) 4, <http://dx.doi.org/10.1504/IJPT.2014.059410>.
- [7] Z. Liu, S. Ihl Woo, Recent advances in catalytic DeNO_x science and technology, *Catal. Rev.* 48 (2006) 43–89, <http://dx.doi.org/10.1080/01614940500439891>.
- [8] L. Lietti, J. Svachula, P. Forzatti, G. Busca, G. Ramis, P. Bregani, Surface and catalytic properties of Vanadia-Titania and Tungsta-Titania systems in the selective catalytic reduction of nitrogen oxides, *Catal. Today* 17 (1993) 131–139, [http://dx.doi.org/10.1016/0920-5861\(93\)80016-T](http://dx.doi.org/10.1016/0920-5861(93)80016-T).
- [9] L.J. Alemany, Reactivity and physicochemical characterization of V₂O₅-WO₃/TiO₂ de-NO_x catalysts, *J. Catal.* 155 (1995) 117–130, <http://dx.doi.org/10.1006/jcat.1995.1193>.
- [10] G. Busca, L. Lietti, G. Ramis, F. Berti, Chemical and mechanistic aspects of the selective catalytic reduction of NO_x by ammonia over oxide catalysts: a review, *Appl. Catal. B Environ.* 18 (1998) 1–36, [http://dx.doi.org/10.1016/S0926-3373\(98\)00040-X](http://dx.doi.org/10.1016/S0926-3373(98)00040-X).
- [11] P. Forzatti, Present status and perspectives in de-NO_x SCR catalysis, *Appl. Catal. A Gen.* 222 (2001) 221–236, [http://dx.doi.org/10.1016/S0926-860X\(01\)00832-8](http://dx.doi.org/10.1016/S0926-860X(01)00832-8).
- [12] P. Forzatti, I. Nova, E. Tronconi, A. Kustov, J.R. Thøgersen, Effect of operating variables on the enhanced SCR reaction over a commercial V₂O₅-WO₃/TiO₂ catalyst for stationary applications, *Catal. Today* 184 (2012) 153–159, <http://dx.doi.org/10.1016/j.cattod.2011.11.006>.

- [13] H. Tschöke, A. Graf, J. Stein, M. Kruger, J. Schaller, N. Breuer, K. Engeljehringer, W. Schindler, Diesel engine exhaust emissions, in: K. Mollenhauer, H. Tschöke (Eds.), *Handbook of Diesel Engines*, Springer, Berlin Heidelberg Berlin, Heidelberg, 2010, pp. 417–486, <http://dx.doi.org/10.1007/978-3-540-89083-6>.
- [14] G. Madia, M. Koebel, M. Elsener, A. Wokaun, Side reactions in the selective catalytic reduction of NO_x with various NO₂ fractions, *Ind. Eng. Chem. Res.* 41 (2002) 4008–4015, <http://dx.doi.org/10.1021/ie020054c>.
- [15] G. Madia, M. Koebel, M. Elsener, A. Wokaun, Side reactions in the selective catalytic reduction of NO_x with various NO₂ fractions, *Ind. Eng. Chem. Res.* 41 (2002) 4008–4015, <http://dx.doi.org/10.1021/ie020054c>.
- [16] M. Yates, J.A. Martín, M.Á. Martín-Luengo, S. Suárez, J. Blanco, N₂O formation in the ammonia oxidation and in the SCR process with V₂O₅-WO₃ catalysts, *Catal. Today* 107–108 (2005) 120–125, <http://dx.doi.org/10.1016/j.cattod.2005.07.015>.
- [17] M.H. Kim, S.-W. Ham, Determination of N₂O emissions levels in the selective reduction of NO_x by NH₃ over an on-site-used commercial V₂O₅-WO₃/TiO₂ catalyst using a modified gas cell, *Top. Catal.* 53 (2010) 597–607, <http://dx.doi.org/10.1007/s11244-010-9493-9>.
- [18] S.G. Lee, H.J. Lee, I. Song, S. Youn, D.H. Kim, S.J. Cho, Suppressed N₂O formation during NH₃ selective catalytic reduction using vanadium on zeolitic microporous TiO₂, *Sci. Rep.* 5 (2015) 12702, <http://dx.doi.org/10.1038/srep12702>.
- [19] A. Chakrabarti, M.E. Ford, D. Gregory, R. Hu, C.J. Keturakis, S. Lwin, Y. Tang, Z. Yang, M. Zhu, M.A. Bañares, I.E. Wachs, A decade+ of operando spectroscopy studies, *Catal. Today* 283 (2017) 27–53, <http://dx.doi.org/10.1016/j.cattod.2016.12.012>.
- [20] L. Arnarson, H. Falsig, S.B. Rasmussen, J.V. Lauritsen, P.G. Moses, A complete reaction mechanism for standard and fast selective catalytic reduction of nitrogen oxides on low coverage VO_x/TiO₂(001) catalysts, *J. Catal.* 346 (2017) 188–197, <http://dx.doi.org/10.1016/j.jcat.2016.12.017>.
- [21] A. Marberger, D. Ferri, M. Elsener, O. Krocher, The significance of lewis acid sites for the selective catalytic reduction of nitric oxide on vanadium-based catalysts, *Angew. Chemie Int. Ed.* 55 (2016) 11989–11994, <http://dx.doi.org/10.1002/anie.201605397>.
- [22] F.J.J.G. Janssen, F.M.G. Van Den Kerkhof, H. Bosch, J.R.H. Ross, Mechanism of the reaction of nitric oxide, ammonia, and oxygen over vanadia catalysts 2. isotopic transient studies with oxygen-18 and nitrogen-15, *J. Phys. Chem.* 91 (1987) 6633–6638, <http://dx.doi.org/10.1021/j100311a016>.
- [23] U.S. Ozkan, M.W. Kumthekar, Y.P. Cai, Selective catalytic reduction of nitric oxide over Vanadia/Titania catalysts: temperature-programmed desorption and isotopically labeled oxygen-Exchange studies, *Ind. Eng. Chem. Res.* 33 (1994) 2924–2929, <http://dx.doi.org/10.1021/ie00036a005>.
- [24] U.S. Ozkan, Y. Cai, M.W. Kumthekar, Mechanistic studies of selective catalytic reduction of nitric oxide with ammonia over V₂O₅/TiO₂ (anatase) catalysts through transient isotopic labeling at steady state, *J. Phys. Chem.* 99 (1995) 2363–2371, <http://dx.doi.org/10.1021/j100008a019>.
- [25] B.L. Duffy, H.E. Curry-Hyde, N.W. Cant, P.F. Nelson, Isotopic labeling studies of the effects of temperature, water, and vanadia loading on the selective catalytic reduction of NO with NH₃ over Vanadia-Titania catalysts, *J. Phys. Chem.* 98 (1994) 7153–7161, <http://dx.doi.org/10.1021/j100080a010>.
- [26] U.S. Ozkan, Y. Cai, M.W. Kumthekar, Investigation of the reaction pathways in selective catalytic reduction of NO with NH₃ over V₂O₅ catalysts: isotopic labeling studies using ¹⁸O₂ ¹⁵NH₃, ¹⁵NO, and ¹⁵N₂O, *J. Catal.* 149 (1994) 390–403, <http://dx.doi.org/10.1006/jcat.1994.1306>.
- [27] N.-Y. Topsøe, T. Slabæk, B.S. Clausena, T.Z. Srnak, J.A. Dumesic, Influence of water on the reactivity of vanadia/titania for catalytic reduction of NO_x, *J. Catal.* 746 (1992) 742–746, [http://dx.doi.org/10.1016/0021-9517\(92\)90358-O](http://dx.doi.org/10.1016/0021-9517(92)90358-O).
- [28] M.D. Amiridis, I.E. Wachs, G. Deo, J.-M. Jehng, D.S. Kim, Reactivity of V₂O₅ catalysts for the selective catalytic reduction of NO by NH₃: influence of vanadia loading, H₂O, and SO₂, *J. Catal.* 161 (1996) 247–253, <http://dx.doi.org/10.1006/jcat.1996.0182>.
- [29] G.T. Went, L.-J. Leu, R.R. Rosin, A.T. Bell, The effects of structure on the catalytic activity and selectivity of V₂O₅/TiO₂ for the reduction of NO by NH₃, *J. Catal.* 134 (1992) 492–505, [http://dx.doi.org/10.1016/0021-9517\(92\)90337-H](http://dx.doi.org/10.1016/0021-9517(92)90337-H).
- [30] C.U.I. Odenbrand, P.L.T. Gabrielsson, J.G.M. Brandin, L.A.H. Andersson, Effect of water vapor on the selectivity in the reduction of nitric oxide with ammonia over vanadia supported on silica-titania, *Appl. Catal.* 78 (1991) 109–122, [http://dx.doi.org/10.1016/0166-9834\(91\)80092-B](http://dx.doi.org/10.1016/0166-9834(91)80092-B).
- [31] Y. He, M.E. Ford, M. Zhu, Q. Liu, Z. Wu, I.E. Wachs, Selective catalytic reduction of NO by NH₃ with WO₃-TiO₂ catalysts: influence of catalyst synthesis method, *Appl. Catal. B Environ.* 188 (2016) 122–133, <http://dx.doi.org/10.1016/j.apcatb.2016.01.072>.
- [32] Y. He, M.E. Ford, M. Zhu, Q. Liu, U. Tumuluri, Z. Wu, I.E. Wachs, Influence of catalyst synthesis method on selective catalytic reduction (SCR) of NO by NH₃ with V₂O₅-WO₃/TiO₂ catalysts, *Appl. Catal. B Environ.* 193 (2016) 141–150, <http://dx.doi.org/10.1016/j.apcatb.2016.04.022>.
- [33] M. Zhu, J.-K. Lai, U. Tumuluri, Z. Wu, I.E. Wachs, Nature of active sites and surface intermediates during SCR of NO with NH₃ by supported V₂O₅-WO₃/TiO₂ Catalysts, *J. Am. Chem. Soc.* (2017), <http://dx.doi.org/10.1021/jacs.7b09646>.